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(54) Title: ZEOLITE CIT-5

(57) Abstract

The present invention relates to new crystalline zeolite CIT-5 prepared using a N(16) methylsparteinium cation templating agent.

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1

ZEOLITE CIT-5

2

This application is a continuation-in-part of application Serial No. 08/910,770, filed
3 August 13, 1997 which is incorporated herein by reference.

4

BACKGROUND OF THE INVENTION

5

Field of the Invention

6

The present invention relates to new crystalline zeolite CIT-5, a method for
7 preparing CIT-5 using a N(16) methylsparteinium cation templating agent, and processes
8 employing CIT-5 as a catalyst.

9

State of the Art

10

Because of their unique sieving characteristics, as well as their catalytic properties,
11 crystalline molecular sieves and zeolites are especially useful in applications such as
12 hydrocarbon conversion, gas drying and separation. Although many different crystalline
13 molecular sieves have been disclosed, there is a continuing need for new zeolites with
14 desirable properties for gas separation and drying, hydrocarbon and chemical conversions,
15 and other applications. New zeolites may contain novel internal pore architectures,
16 providing enhanced selectivities in these processes.

17

SUMMARY OF THE INVENTION

18

The present invention is directed to a family of crystalline molecular sieves with
19 unique properties, referred to herein as "zeolite CIT-5" or simply "CIT-5". Preferably, CIT-
20 5 is obtained in its silicate or aluminosilicate form. The term "silicate" refers to a zeolite
21 having a high mole ratio of silicon oxide relative to aluminum oxide, preferably a mole ratio
22 greater than about 100. As used herein, the term "aluminosilicate" refers to a zeolite
23 containing both alumina and silica.

24

In accordance with this invention, there is provided a zeolite comprising an oxide of
25 a tetravalent element or mixture of oxides of tetravalent elements and, optionally, an oxide
26 of a trivalent element or mixtures of oxides of trivalent elements and having, after
27 calcination, the X-ray diffraction lines of Table II.

28

Further, in accordance with this invention, there is provided a zeolite comprising an
29 oxide selected from silicon oxide, germanium oxide and mixtures thereof and an optional
30 oxide selected from aluminum oxide, boron oxide, gallium oxide, iron oxide and mixtures
31 thereof and having, after calcination, the X-ray diffraction lines of Table II below.

32

The present invention further provides such a zeolite having a composition, as

1 synthesized and in the anhydrous state, in terms of mole ratios as follows:

2 $\text{YO}_2/\text{W}_a\text{O}_b$ > 40

3 M/YO₂ ≤ 0.05

4 Q/YO₂ ≤ 0.05

5 wherein Y is silicon, germanium or a mixture thereof; W is aluminum, boron, gallium, iron
6 or mixtures thereof; a= 1 or 2, b=2 when a=1 (i.e., W is tetravalent) and b=3 when a=2 (i.e.,
7 W is trivalent); M is an alkali metal; and Q comprises a N(16) methylsparteinium cation.

8 In accordance with this invention, there is provided a zeolite comprising an oxide of
9 silicon, germanium or mixtures thereof and an oxide of titanium and having, after
10 calcination, the X-ray diffraction lines of Table II.

11 The present invention also provides a zeolite having a composition, as synthesized
12 and in the anhydrous state, in terms of mole ratios as follows:

13 YO_2/TiO_2 > 40

14 M/YO₂ ≤ 0.05

15 Q/YO₂ ≤ 0.05

16 wherein Y is silicon, germanium or a mixture thereof; M is an alkali metal; and Q
17 comprises a N(16) methylsparteinium cation.

18 In accordance with this invention, there is also provided a zeolite prepared by
19 thermally treating a zeolite comprising an oxide selected from silicon oxide, germanium
20 oxide and mixtures thereof and, optionally, an oxide selected from aluminum oxide, boron
21 oxide, gallium oxide, iron oxide and mixtures thereof at a temperature of from about 200°C
22 to about 800°C, the thus-prepared zeolite having the X-ray diffraction lines of Table II. The
23 present invention also includes this thus-prepared zeolite which is predominantly in the
24 hydrogen form, which hydrogen form is prepared by ion exchanging with an acid or with a
25 solution of an ammonium salt followed by a second calcination.

26 Also provided in accordance with the present invention is a method of preparing a
27 crystalline material comprising an oxide of a tetravalent element or mixture of oxides of
28 tetravalent elements and, optionally, an oxide of a trivalent element or mixtures of oxides of
29 trivalent elements, said method comprising contacting in admixture under crystallization
30 conditions sources of said oxides, a source of alkali metal and a templating agent comprising
31 a N(16) methylsparteinium cation.

32 The present invention additionally provides a process for converting hydrocarbons

1 comprising contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with
2 a catalyst comprising the zeolite of this invention. The zeolite may be predominantly in the
3 hydrogen form, partially acidic or substantially free of acidity, depending on the process.

4 Further provided by the present invention is a hydrocracking process comprising
5 contacting a hydrocarbon feedstock under hydrocracking conditions with a catalyst
6 comprising the zeolite of this invention, preferably predominantly in the hydrogen form.

7 This invention also includes a dewaxing process comprising contacting a
8 hydrocarbon feedstock under dewaxing conditions with a catalyst comprising the zeolite of
9 this invention, preferably predominantly in the hydrogen form.

10 The present invention also includes a process for improving the viscosity index of a
11 dewaxed product of waxy hydrocarbon feeds comprising contacting the waxy hydrocarbon
12 feed under isomerization dewaxing conditions with a catalyst comprising the zeolite of this
13 invention, preferably predominantly in the hydrogen form.

14 The present invention further includes a process for producing a C₂₀₊ lube oil from a
15 C₂₀₊ olefin feed comprising isomerizing said olefin feed under isomerization conditions over
16 a catalyst comprising at least one Group VIII metal and the zeolite of this invention. The
17 zeolite may be predominantly in the hydrogen form.

18 In accordance with this invention, there is also provided a process for catalytically
19 dewaxing a hydrocarbon oil feedstock boiling above about 350°F and containing straight
20 chain and slightly branched chain hydrocarbons comprising contacting said hydrocarbon oil
21 feedstock in the presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi
22 with a catalyst comprising at least one Group VIII metal and the zeolite of this invention,
23 preferably predominantly in the hydrogen form. The catalyst may be a layered catalyst
24 comprising a first layer comprising at least one Group VIII metal and the zeolite of this
25 invention, and a second layer comprising an aluminosilicate zeolite which is more shape
26 selective than the zeolite of said first layer.

27 Also included in the present invention is a process for preparing a lubricating oil
28 which comprises hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to
29 obtain an effluent comprising a hydrocracked oil, and catalytically dewaxing said effluent
30 comprising hydrocracked oil at a temperature of at least about 400°F and at a pressure of
31 from about 15 psig to about 3000 psig in the presence of added hydrogen gas with a catalyst
32 comprising at least one Group VIII metal and the zeolite of this invention. The zeolite may

1 be predominantly in the hydrogen form.

2 Further included in this invention is a process for isomerization dewaxing a raffinate
3 comprising contacting said raffinate in the presence of added hydrogen with a catalyst
4 comprising at least one Group VIII metal and the zeolite of this invention. The raffinate
5 may be bright stock, and the zeolite may be predominantly in the hydrogen form.

6 Also included in this invention is a process for increasing the octane of a
7 hydrocarbon feedstock to produce a product having an increased aromatics content
8 comprising contacting a hydrocarbonaceous feedstock which comprises normal and slightly
9 branched hydrocarbons having a boiling range above about 40°C and less than about 200°C,
10 under aromatic conversion conditions with a catalyst comprising the zeolite of this invention
11 made substantially free of acidity by neutralizing said zeolite with a basic metal. Also
12 provided in this invention is such a process wherein the zeolite contains a Group VIII metal
13 component.

14 Also provided by the present invention is a catalytic cracking process comprising
15 contacting a hydrocarbon feedstock in a reaction zone under catalytic cracking conditions in
16 the absence of added hydrogen with a catalyst comprising the zeolite of this invention,
17 preferably predominantly in the hydrogen form. Also included in this invention is such a
18 catalytic cracking process wherein the catalyst additionally comprises a large pore crystalline
19 cracking component.

20 This invention further provides an isomerization process for isomerizing C₄ to C₇
21 hydrocarbons, comprising contacting a feed having normal and slightly branched C₄ to C₇
22 hydrocarbons under isomerizing conditions with a catalyst comprising the zeolite of this
23 invention, preferably predominantly in the hydrogen form. The zeolite may be impregnated
24 with at least one Group VIII metal, preferably platinum. The catalyst may be calcined in a
25 steam/air mixture at an elevated temperature after impregnation of the Group VIII metal.

26 Also provided by the present invention is a process for alkylating an aromatic
27 hydrocarbon which comprises contacting under alkylation conditions at least a molar excess
28 of an aromatic hydrocarbon with a C₂ to C₂₀ olefin under at least partial liquid phase
29 conditions and in the presence of a catalyst comprising the zeolite of this invention,
30 preferably predominantly in the hydrogen form. The olefin may be a C₂ to C₄ olefin, and the
31 aromatic hydrocarbon and olefin may be present in a molar ratio of about 4:1 to about 20:1,
32 respectively. The aromatic hydrocarbon may be selected from the group consisting of

1 benzene, toluene, ethylbenzene, xylene, or mixtures thereof.

2 Further provided in accordance with this invention is a process for transalkylating an
3 aromatic hydrocarbon which comprises contacting under transalkylating conditions an
4 aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon under at least partial liquid
5 phase conditions and in the presence of a catalyst comprising the zeolite of this invention,
6 preferably predominantly in the hydrogen form. The aromatic hydrocarbon and the
7 polyalkyl aromatic hydrocarbon may be present in a molar ratio of from about 1:1 to about
8 25:1, respectively. The aromatic hydrocarbon may be selected from the group consisting of
9 benzene, toluene, ethylbenzene, xylene, or mixtures thereof, and the polyalkyl aromatic
10 hydrocarbon may be a dialkylbenzene.

11 Further provided by this invention is a process to convert paraffins to aromatics
12 which comprises contacting paraffins under conditions which cause paraffins to convert to
13 aromatics with a catalyst comprising the zeolite of this invention, said catalyst comprising
14 gallium, zinc, or a compound of gallium or zinc.

15 In accordance with this invention there is also provided a process for isomerizing
16 olefins comprising contacting said olefin under conditions which cause isomerization of the
17 olefin with a catalyst comprising the zeolite of this invention.

18 Further provided in accordance with this invention is a process for isomerizing an
19 isomerization feed comprising an aromatic C₈ stream of xylene isomers or mixtures of
20 xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio of ortho-, meta-
21 and para-xlenes is obtained, said process comprising contacting said feed under
22 isomerization conditions with a catalyst comprising the zeolite of this invention.

23 The present invention further provides a process for oligomerizing olefins
24 comprising contacting an olefin feed under oligomerization conditions with a catalyst
25 comprising the zeolite of this invention.

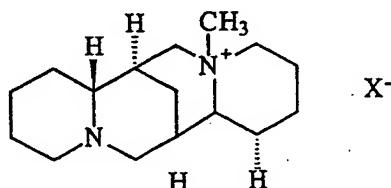
26 This invention also provides a process for converting lower alcohols and other
27 oxygenated hydrocarbons comprising contacting said lower alcohol or other oxygenated
28 hydrocarbon with a catalyst comprising the zeolite of this invention under conditions to
29 produce liquid products.

30 Also provided by the present invention is an improved process for the reduction of
31 oxides of nitrogen contained in a gas stream in the presence of oxygen wherein said process
32 comprises contacting the gas stream with a zeolite, the improvement comprising using as the

1 zeolite, the zeolite of this invention. The zeolite may contain a metal or metal ions (such as
 2 cobalt, copper or mixtures thereof) capable of catalyzing the reduction of the oxides of
 3 nitrogen, and may be conducted in the presence of a stoichiometric excess of oxygen. In a
 4 preferred embodiment, the gas stream is the exhaust stream of an internal combustion
 5 engine.

6 DETAILED DESCRIPTION OF THE INVENTION

7 In preparing CIT-5 zeolites, a N(16) methylsparteinium cation is used as a
 8 crystallization template. The N(16) methylsparteinium cation may have the following
 9 structure:



10
 11 The anion (X⁻) associated with the cation may be any anion which is not detrimental to the
 12 formation of the zeolite. Representative anions include halogen, e.g., fluoride, chloride,
 13 bromide and iodide, hydroxide, acetate, sulfate, tetrafluoroborate, carboxylate, and the like.
 14 Hydroxide is the most preferred anion.

15 The N(16) methylsparteinium cation may be prepared as described in Lobo and
 16 Davis, "Synthesis and Characterization of Pure-Silica and Boron-Substituted SSZ-24 Using
 17 N(16) methylsparteinium Bromide as Structure-Directing Agent", *Microporous Materials 3*
 18 (1994), pp. 61-69, Elsevier.

19 In general, CIT-5 is prepared by contacting an active source of one or more oxides
 20 selected from the group consisting of alkali metal oxide, trivalent element oxide(s), and
 21 tetravalent element oxide(s) with the N(16) methylsparteinium cation templating agent.

22 CIT-5 is prepared from a reaction mixture having the composition shown in Table A
 23 below.

TABLE A

Reaction Mixture

| | | Typical | Preferred (*) |
|---|---------------|---------------|-------------------|
| 3 | | | |
| 4 | YO_2/W_aO_b | 15 - ∞ | 25 - ∞ |
| 5 | OH^-/YO_2 | 0.1 - 0.5 | 0.2 - 0.45 (0.3) |
| 6 | Q/YO_2 | 0.1 - 0.3 | 0.15 - 0.25 (0.2) |
| 7 | M/YO_2 | 0.02 - 0.3 | 0.05 - 0.2 (0.1) |
| 8 | H_2O/YO_2 | 15 - 200 | 30 - 100 (40) |

*Numbers in parentheses represent quantities believed to be optimal.

10 where Y , W , a , b , M and Q are as defined above.

11 It should be emphasized that CIT-5 can be made in its all-silica form, i.e., where a
12 source of another oxide is not intentionally added to the reaction mixture. In this case,
13 $\text{YO}_2/\text{W}_a\text{O}_b$ would be at or near ∞ .

14. In practice, CIT-5 is prepared by a process comprising:

15 (a) preparing an aqueous solution containing sources of at least one oxide
16 capable of forming a crystalline molecular sieve and a N(16) methylsparteinium
17 cation having an anionic counterion which is not detrimental to the formation of
18 CIT-5;

19 (b) maintaining the aqueous solution under conditions sufficient to form crystals
20 of CIT-5; and

21 (c) recovering the crystals of CIT-5.

22 Accordingly, CIT-5 may comprise the crystalline material and the templating agent
23 in combination with metallic and non-metallic oxides bonded in tetrahedral coordination
24 through shared oxygen atoms to form a cross-linked three dimensional crystal structure.

25 The metallic and non-metallic oxides comprise one or a combination of oxides of a
26 tetravalent element(s), and, optionally, one or a combination of a trivalent element(s). The
27 tetravalent element(s) is preferably selected from the group consisting of silicon, germanium
28 and combinations thereof. More preferably, the tetravalent element is silicon. The trivalent
29 element is preferably aluminum, boron, gallium, or iron . In terms of reaction speed,
30 gallium is preferred. However, in some catalytic applications, aluminum is preferred.

31 Typical sources of aluminum oxide for the reaction mixture include aluminates,
32 alumina, aluminum colloids, aluminum oxide coated on silica sol, hydrated alumina gels

1 such as $\text{Al}(\text{OH})_3$ and aluminum compounds such as AlCl_3 and $\text{Al}_2(\text{SO}_4)_3$. Typical sources
2 of silicon oxide include silicates, silica hydrogel, silicic acid, fumed silica, colloidal silica,
3 tetra-alkyl orthosilicates, and silica hydroxides.

4 A source zeolite reagent may provide a source of aluminum. In most cases, the
5 source zeolite also provides a source of silica. The source zeolite in its dealuminated or
6 form may also be used as a source of silica, with additional silicon added using, for
7 example, the conventional sources listed above. Use of a source zeolite reagent as a source
8 of alumina for the present process is more completely described in U.S. Patent
9 No. 5,225,179, issued July 6, 1993 to Zones et al. entitled "Method of Making Molecular
10 Sieves", the disclosure of which is incorporated herein by reference.

11 An alkali metal is added to the reaction mixture. A variety of sources can be used,
12 such as alkali metal hydroxides and alkali metal carbonates. Lithium or a mixture of lithium
13 and another alkali metal is preferred, with lithium hydroxide being particularly preferred.
14 The lithium cation may be part of the as-synthesized crystalline oxide material, in order to
15 balance valence electron charges therein. Other alkali metals which can be used include
16 sodium and potassium, with the hydroxides being preferred. The alkali metal may be
17 employed in an amount of from about 0.03 to about 0.15 mole of alkali metal per mole of
18 silica (or other oxide(s) of a tetravalent element(s)).

19 It has been found that the inclusion of zinc in the reaction mixture can help prevent
20 the formation of crystal phases other than the CIT-5. The zinc can be added as, e.g., zinc
21 acetate dihydrate, in an amount of up to about 0.08, preferably about 0.04, mole of zinc
22 acetate dihydrate per mole of silica (or other oxide(s) of a tetravalent element(s)).

23 The reaction mixture is maintained at an elevated temperature until the crystals of
24 the CIT-5 zeolite are formed. The hydrothermal crystallization is usually conducted under
25 autogenous pressure, at a temperature between 100°C and 200°C, preferably between 135°C
26 and 160°C. The crystallization period is typically greater than 1 day and preferably from
27 about 7 days to about 21 days.

28 During the hydrothermal crystallization step, the CIT-5 crystals can be allowed to
29 nucleate spontaneously from the reaction mixture. The use of CIT-5 crystals as seed
30 material can be advantageous in decreasing the time necessary for complete crystallization
31 to occur. In addition, seeding can lead to an increased purity of the product obtained by
32 promoting the nucleation and/or formation of CIT-5 over any undesired phases. When used

1 as seeds, CIT-5 crystals are added in an amount between 0.1 and 10% of the weight of silica
2 used in the reaction mixture.

3 Once the zeolite crystals have formed, the solid product is separated from the
4 reaction mixture by standard mechanical separation techniques such as filtration. The
5 crystals are water-washed and then dried, e.g., at 90°C to 150°C for from 8 to 24 hours, to
6 obtain the as-synthesized CIT-5 zeolite crystals. The drying step can be performed at
7 atmospheric pressure or under vacuum.

8 CIT-5 has a composition, as synthesized and in the anhydrous state, in terms of mole
9 ratios, shown in Table B below.

10 TABLE B
11 As-Synthesized CIT-5

| | | |
|----|--|--------|
| 12 | YO ₂ /W _a O _b | > 40 |
| 13 | M/YO ₂ | ≤ 0.05 |
| 14 | Q/YO ₂ | ≤ 0.05 |

15 where Y, W, a, b, M and Q are as defined above. As noted above, CIT-5 can be in the all-
16 silica form, in which case YO₂/W_aO_b would be at or near ∞ .

17 Lower silica to alumina ratios may also be obtained by using methods which insert
18 aluminum into the crystalline framework. For example, aluminum insertion may occur by
19 thermal treatment of the zeolite in combination with an alumina binder or dissolved source
20 of alumina. Such procedures are described in U.S. Patent No. 4,559,315, issued on
21 December 17, 1985 to Chang et al.

22 It is believed that CIT-5 is comprised of a new framework structure or topology
23 which is characterized by its X-ray diffraction pattern. CIT-5 zeolites, as-synthesized, have
24 a crystalline structure whose X-ray powder diffraction pattern typically exhibits the
25 characteristic lines shown in Table I and are thereby distinguished from other known
26 zeolites.

1

TABLE I

2

As-Synthesized All-Silica CIT-5

| <u>2 Theta^(a)</u> | <u>d</u> | <u>Relative Intensity^(b)</u> |
|------------------------------|----------|---|
| 6.96 | 12.7 | VS |
| 7.29 | 12.12 | S |
| 12.81 | 6.905 | W |
| 13.93 | 6.353 | M |
| 18.96 | 4.676 | S |
| 19.59 | 4.528 | M |
| 20.00 | 4.436 | S |
| 20.50 | 4.329 | M-S |
| 20.95 | 4.236 | S-VS |
| 21.93 | 4.050 | W |
| 23.41 | 3.797 | W |
| 24.22 | 3.672 | W |
| 24.62 | 3.612 | M |
| 25.80 | 3.451 | W |
| 26.10 | 3.412 | W |
| 26.73 | 3.332 | S-VS |
| 27.11 | 3.286 | W |
| 28.22 | 3.159 | M |
| 29.38 | 3.038 | W |
| 29.82 | 2.994 | W |
| 31.37 | 2.849 | W |
| 31.55 | 2.833 | W |
| 32.99 | 2.713 | W |
| 33.98 | 2.636 | W |
| 35.33 | 2.538 | W |
| 35.64 | 2.517 | W |
| 36.42 | 2.465 | W |
| 37.03 | 2.426 | W |
| 37.70 | 2.384 | W |
| 38.73 | 2.323 | W |
| 44.70 | 2.026 | W |

| | | | |
|---|------------------------------------|-------|---|
| 1 | 49.42 ^(a) ± 0.15 | 1.843 | W |
|---|------------------------------------|-------|---|

(b) The X-ray patterns provided are based on a relative intensity scale in which the strongest line in the X-ray pattern is assigned a value of 100: W(weak) is less than 20; M(medium) is between 20 and 40; S(strong) is between 40 and 60; VS(very strong) is greater than 60.

After calcination, the CIT-5 zeolites have a crystalline structure whose X-ray powder diffraction pattern typically includes the characteristic lines shown in Table II:

8 TABLE II
 9 Calcined CIT-5

| <u>2 Theta^(a)</u> | <u>d</u> | <u>Relative Intensity</u> |
|------------------------------|----------|---------------------------|
| 6.95 | 12.7 | VS |
| 7.3 | 12.1 | S-VS |
| 13.9 | 6.37 | W-S |
| 19.0 | 4.67 | W-VS |
| 20.0 | 4.44 | M-VS |
| 20.5 | 4.33 | W-S |
| 20.9 | 4.25 | W-VS |
| 24.6 | 3.62 | W-M |
| 26.8 | 3.32 | W-VS |

10 (a) ± 0.15

11 Table IIA below shows the X-ray powder diffraction lines for calcined CIT-5
12 including actual relative intensities.

13 TABLE II A
 14 Calcined CIT-5

| <u>2 Theta^(a)</u> | <u>d</u> | <u>Relative Intensity</u> |
|------------------------------|----------|---------------------------|
| 6.95 | 12.7 | 65-100 |
| 7.3 | 12.1 | 40-100 |
| 13.9 | 6.37 | 1-65 |
| 19.0 | 4.67 | 10-100 |
| 20.0 | 4.44 | 20-70 |
| 20.5 | 4.33 | 10-50 |
| 20.9 | 4.25 | 5-100 |

| | | | |
|---|-----------------------|------|-------|
| | 24.6 | 3.62 | 5-45 |
| | 26.8 | 3.32 | 10-70 |
| 1 | ^(a) ± 0.15 | | |

2 The X-ray powder diffraction patterns were determined by standard techniques. The
3 radiation was the K-alpha/doublet of copper. The peak heights and the positions, as a
4 function of 2θ where θ is the Bragg angle, were read from the relative intensities of the
5 peaks, and d , the interplanar spacing in Angstroms corresponding to the recorded lines, can
6 be calculated.

7 The variation in the scattering angle (two theta) measurements, due to instrument
8 error and to differences between individual samples, is estimated at ± 0.15 degrees.

9 The X-ray diffraction pattern of Table I is representative of "as-synthesized" or
10 "as-made" CIT-5 zeolites. Minor variations in the diffraction pattern can result from
11 variations in the, e.g., silica-to-alumina mole ratio of the particular sample due to changes in
12 lattice constants. In addition, sufficiently small crystals will affect the shape and intensity of
13 peaks, leading to significant peak broadening.

14 Representative peaks from the X-ray diffraction pattern of calcined CIT-5 are shown
15 in Table II. Calcination can also result in changes in the intensities of the peaks as
16 compared to patterns of the "as-made" material, as well as minor shifts in the diffraction
17 pattern. The zeolite produced by exchanging the metal or other cations present in the zeolite
18 with various other cations (such as H^+ or NH_4^+) yields essentially the same diffraction
19 pattern, although again, there may be minor shifts in the interplanar spacing and variations
20 in the relative intensities of the peaks. Notwithstanding these minor perturbations, the basic
21 crystal lattice remains unchanged by these treatments.

22 Crystalline CIT-5 can be used as-synthesized, but preferably will be thermally treated
23 (calcined). Usually, it is desirable to remove the alkali metal cation by ion exchange and
24 replace it with hydrogen, ammonium, or any desired metal ion. The zeolite can be leached
25 with chelating agents, e.g., EDTA or dilute acid solutions, to increase the silica to alumina
26 mole ratio. The zeolite can also be steamed; steaming helps stabilize the crystalline lattice
27 to attack from acids.

28 The zeolite can be used in intimate combination with hydrogenating components,
29 such as tungsten, vanadium molybdenum, rhenium, nickel cobalt, chromium, manganese, or
30 a noble metal, such as palladium or platinum, for those applications in which a

1 hydrogenation-dehydrogenation function is desired.

2 Metals may also be introduced into the zeolite by replacing some of the cations in
3 the zeolite with metal cations via standard ion exchange techniques (see, for example, U.S.
4 Patent Nos. 3,140,249 issued July 7, 1964 to Plank et al.; 3,140,251 issued July 7, 1964 to
5 Plank et al.; and 3,140,253 issued July 7, 1964 to Plank et al.). Typical replacing cations
6 can include metal cations, e.g., rare earth, Group IA, Group IIA and Group VIII metals, as
7 well as their mixtures. Of the replacing metallic cations, cations of metals such as rare
8 earth, Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, and Fe are particularly preferred.

9 The hydrogen, ammonium, and metal components can be ion-exchanged into the
10 CIT-5. The zeolite can also be impregnated with the metals, or, the metals can be physically
11 and intimately admixed with the zeolite using standard methods known to the art.

12 Typical ion-exchange techniques involve contacting the synthetic zeolite with a
13 solution containing a salt of the desired replacing cation or cations. Although a wide variety
14 of salts can be employed, chlorides and other halides, acetates, nitrates, and sulfates are
15 particularly preferred. The zeolite is usually calcined prior to the ion-exchange procedure to
16 remove the organic matter present in the channels and on the surface, since this results in a
17 more effective ion exchange. Representative ion exchange techniques are disclosed in a
18 wide variety of patents including U.S. Patent Nos. 3,140,249 issued on July 7, 1964 to Plank
19 et al.; 3,140,251 issued on July 7, 1964 to Plank et al.; and 3,140,253 issued on July 7, 1964
20 to Plank et al.

21 Following contact with the salt solution of the desired replacing cation, the zeolite is
22 typically washed with water and dried at temperatures ranging from 65°C to about 200°C.
23 After washing, the zeolite can be calcined in air or inert gas at temperatures ranging from
24 about 200°C to about 800°C for periods of time ranging from 1 to 48 hours, or more, to
25 produce a catalytically active product especially useful in hydrocarbon conversion processes.

26 Regardless of the cations present in the synthesized form of CIT-5, the spatial
27 arrangement of the atoms which form the basic crystal lattice of the zeolite remains
28 essentially unchanged.

29 CIT-5 can be formed into a wide variety of physical shapes. Generally speaking, the
30 zeolite can be in the form of a powder, a granule, or a molded product, such as extrudate
31 having a particle size sufficient to pass through a 2-mesh (Tyler) screen and be retained on a
32 400-mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion with

1 an organic binder, the aluminosilicate can be extruded before drying, or, dried or partially
2 dried and then extruded.

3 CIT-5 can be composited with other materials resistant to the temperatures and other
4 conditions employed in organic conversion processes. Such matrix materials include active
5 and inactive materials and synthetic or naturally occurring zeolites as well as inorganic
6 materials such as clays, silica and metal oxides. Examples of such materials and the manner
7 in which they can be used are disclosed in U.S. Patent No. 4,910,006, issued May 20, 1990
8 to Zones et al., and U.S. Patent No. 5,316,753, issued May 31, 1994 to Nakagawa, both of
9 which are incorporated by reference herein in their entirety.

10 Hydrocarbon Conversion Processes

11 CIT-5 zeolites are useful in hydrocarbon conversion reactions. Hydrocarbon
12 conversion reactions are chemical and catalytic processes in which carbon containing
13 compounds are changed to different carbon containing compounds. Examples of
14 hydrocarbon conversion reactions in which CIT-5 are expected to be useful include
15 hydrocracking, dewaxing, catalytic cracking and olefin and aromatics formation reactions.
16 The catalysts are also expected to be useful in other petroleum refining and hydrocarbon
17 conversion reactions such as isomerizing n-paraffins and naphthenes, polymerizing and
18 oligomerizing olefinic or acetylenic compounds such as isobutylene and butene-1,
19 reforming, isomerizing polyalkyl substituted aromatics (e.g., m-xylene), and
20 disproportionating aromatics (e.g., toluene) to provide mixtures of benzene, xylenes and
21 higher methylbenzenes and oxidation reactions. Also included are rearrangement reactions
22 to make various naphthalene derivatives. The CIT-5 catalysts may have high selectivity, and
23 under hydrocarbon conversion conditions can provide a high percentage of desired products
24 relative to total products.

25 CIT-5 zeolites can be used in processing hydrocarbonaceous feedstocks.
26 Hydrocarbonaceous feedstocks contain carbon compounds and can be from many different
27 sources, such as virgin petroleum fractions, recycle petroleum fractions, shale oil, liquefied
28 coal, tar sand oil, synthetic paraffins from NAO, recycled plastic feedstocks and, in general,
29 can be any carbon containing feedstock susceptible to zeolitic catalytic reactions.
30 Depending on the type of processing the hydrocarbonaceous feed is to undergo, the feed can
31 contain metal or be free of metals, it can also have high or low nitrogen or sulfur impurities.
32 It can be appreciated, however, that in general processing will be more efficient (and the

1 catalyst more active) the lower the metal, nitrogen, and sulfur content of the feedstock.

2 The conversion of hydrocarbonaceous feeds can take place in any convenient mode,
 3 for example, in fluidized bed, moving bed, or fixed bed reactors depending on the types of
 4 process desired. The formulation of the catalyst particles will vary depending on the
 5 conversion process and method of operation.

6 Other reactions which can be performed using the catalyst of this invention
 7 containing a metal, e.g., a Group VIII metal such platinum, include
 8 hydrogenation-dehydrogenation reactions, denitrogenation and desulfurization reactions.

9 Depending upon the type of reaction which is catalyzed, the zeolite may be
 10 predominantly in the hydrogen form, partially acidic or substantially free of acidity. As used
 11 herein, "predominantly in the hydrogen form" means that, after calcination, at least 80% of
 12 the cation sites are occupied by hydrogen ions and/or rare earth ions.

13 The following table indicates typical reaction conditions which may be employed
 14 when using catalysts comprising CIT-5 in the hydrocarbon conversion reactions of this
 15 invention. Preferred conditions are indicated in parentheses.

| Process | Temp.,°C | Pressure | LHSV |
|--------------------------|---|---|--|
| Hydrocracking | 175-485 | 0.5-350 bar | 0.1-30 |
| Dewaxing | 200-475 (250-450) | 15-3000 psig (200-3000) | 0.1-20 (0.2-10) |
| Aromatics formation | 400-600 (480-550) | atm.-10 bar | 0.1-15 |
| Cat. cracking | 127-885 | subatm. ¹ (atm.-5 atm.) | 0.5-50 |
| Oligomerization | 232-649 ² 10-232 ⁴ (27-204) ⁴ | 0.1-50 atm. ^{2,3} | 0.2-50 ² 0.05-20 ⁵ (0.1-10) ⁵ |
| Paraffins to aromatics | 100-700 | 0-1000 psig | 0.5-40 ⁵ |
| Condensation of alcohols | 260-538 | 0.5-1000 psig | 0.5-50 ⁵ |
| Isomerization | 93-538 (204-315) | 50-1000 psig | 1-10 (1-4) |
| Xylene isomerization | 260-593 ² (315-566) ² 38-371 ⁴ | 0.5-50 atm. ² (1-5 atm) ² 1-200 atm. ⁴ | 0.1-100 ⁵ (0.5-50) ⁵ 0.5-50 |

16 ¹ Several hundred atmospheres

17 ² Gas phase reaction

18 ³ Hydrocarbon partial pressure

19 ⁴ Liquid phase reaction

20 ⁵ WHSV

1 Other reaction conditions and parameters are provided below.

2 Hydrocracking

3 Using a catalyst which comprises CIT-5, preferably predominantly in the hydrogen
4 form, and a hydrogenation promoter, heavy petroleum residual feedstocks, cyclic stocks and
5 other hydrocrackate charge stocks can be hydrocracked using the process conditions and
6 catalyst components disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S.
7 Patent No. 5,316,753.

8 The hydrocracking catalysts contain an effective amount of at least one
9 hydrogenation component of the type commonly employed in hydrocracking catalysts. The
10 hydrogenation component is generally selected from the group of hydrogenation catalysts
11 consisting of one or more metals of Group VIB and Group VIII, including the salts,
12 complexes and solutions containing such. The hydrogenation catalyst is preferably selected
13 from the group of metals, salts and complexes thereof of the group consisting of at least one
14 of platinum, palladium, rhodium, iridium, ruthenium and mixtures thereof or the group
15 consisting of at least one of nickel, molybdenum, cobalt, tungsten, titanium, chromium and
16 mixtures thereof. Reference to the catalytically active metal or metals is intended to
17 encompass such metal or metals in the elemental state or in some form such as an oxide,
18 sulfide, halide, carboxylate and the like. The hydrogenation catalyst is present in an
19 effective amount to provide the hydrogenation function of the hydrocracking catalyst, and
20 preferably in the range of from 0.05 to 25% by weight.

21 Dewaxing

22 CIT-5, preferably predominantly in the hydrogen form, can be used to dewax
23 hydrocarbonaceous feeds by selectively removing straight chain paraffins. Typically, the
24 viscosity index of the dewaxed product is improved (compared to the waxy feed) when the
25 waxy feed is contacted with CIT-5 under isomerization dewaxing conditions.

26 The catalytic dewaxing conditions are dependent in large measure on the feed used
27 and upon the desired pour point. Hydrogen is preferably present in the reaction zone during
28 the catalytic dewaxing process. The hydrogen to feed ratio is typically between about 500
29 and about 30,000 SCF/bbl (standard cubic feet per barrel), preferably about 1000 to about
30 20,000 SCF/bbl. Generally, hydrogen will be separated from the product and recycled to the
31 reaction zone. Typical feedstocks include light gas oil, heavy gas oils and reduced crudes
32 boiling above about 350°F.

1 A typical dewaxing process is the catalytic dewaxing of a hydrocarbon oil feedstock
2 boiling above about 350°F and containing straight chain and slightly branched chain
3 hydrocarbons by contacting the hydrocarbon oil feedstock in the presence of added hydrogen
4 gas at a hydrogen pressure of about 15-3000 psi with a catalyst comprising CIT-5 and at
5 least one Group VIII metal.

6 The CIT-5 hydrodewaxing catalyst may optionally contain a hydrogenation
7 component of the type commonly employed in dewaxing catalysts. See the aforementioned
8 U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for examples of these
9 hydrogenation components.

10 The hydrogenation component is present in an effective amount to provide an
11 effective hydrodewaxing and hydroisomerization catalyst preferably in the range of from
12 about 0.05 to 5% by weight. The catalyst may be run in such a mode to increase
13 isodewaxing at the expense of cracking reactions.

14 The feed may be hydrocracked, followed by dewaxing. This type of two stage
15 process and typical hydrocracking conditions are described in U.S. Patent No. 4,921,594,
16 issued May 1, 1990 to Miller, which is incorporated herein by reference in its entirety.

17 CIT-5 may also be utilized as a dewaxing catalyst in the form of a layered catalyst.
18 That is, the catalyst comprises a first layer comprising zeolite CIT-5 and at least one
19 Group VIII metal, and a second layer comprising an aluminosilicate zeolite which is more
20 shape selective than zeolite CIT-5. The use of layered catalysts is disclosed in U.S. Patent
21 No. 5,149,421, issued September 22, 1992 to Miller, which is incorporated by reference
22 herein in its entirety. The layering may also include a bed of CIT-5 layered with a non-
23 zeolitic component designed for either hydrocracking or hydrofinishing.

24 CIT-5 may also be used to dewax raffinates, including bright stock, under conditions
25 such as those disclosed in U. S. Patent No. 4,181,598, issued January 1, 1980 to Gillespie
26 et al., which is incorporated by reference herein in its entirety.

27 It is often desirable to use mild hydrogenation (sometimes referred to as
28 hydrofinishing) to produce more stable dewaxed products. The hydrofinishing step can be
29 performed either before or after the dewaxing step, and preferably after. Hydrofinishing is
30 typically conducted at temperatures ranging from about 190°C to about 340°C at pressures
31 from about 400 psig to about 3000 psig at space velocities (LHSV) between about 0.1 and
32 20 and a hydrogen recycle rate of about 400 to 1500 SCF/bbl. The hydrogenation catalyst

1 employed must be active enough not only to hydrogenate the olefins, diolefins and color
2 bodies which may be present, but also to reduce the aromatic content. Suitable
3 hydrogenation catalyst are disclosed in U. S. Patent No. 4,921,594, issued May 1, 1990 to
4 Miller, which is incorporated by reference herein in its entirety. The hydrofinishing step is
5 beneficial in preparing an acceptably stable product (e.g., a lubricating oil) since dewaxed
6 products prepared from hydrocracked stocks tend to be unstable to air and light and tend to
7 form sludges spontaneously and quickly.

8 Lube oil may be prepared using CIT-5. For example, a C₂₀₊ lube oil may be made by
9 isomerizing a C₂₀₊ olefin feed over a catalyst comprising CIT-5 in the hydrogen form and at
10 least one Group VIII metal. Alternatively, the lubricating oil may be made by hydrocracking
11 in a hydrocracking zone a hydrocarbonaceous feedstock to obtain an effluent comprising a
12 hydrocracked oil, and catalytically dewaxing the effluent at a temperature of at least about
13 400°F and at a pressure of from about 15 psig to about 3000 psig in the presence of added
14 hydrogen gas with a catalyst comprising CIT-5 in the hydrogen form and at least one
15 Group VIII metal.

16 Aromatics Formation

17 CIT-5 can be used to convert light straight run naphthas and similar mixtures to
18 highly aromatic mixtures. Thus, normal and slightly branched chained hydrocarbons,
19 preferably having a boiling range above about 40°C and less than about 200°C, can be
20 converted to products having a substantial higher octane aromatics content by contacting the
21 hydrocarbon feed with a catalyst comprising CIT-5. It is also possible to convert heavier
22 feeds into BTX or naphthalene derivatives of value using a catalyst comprising CIT-5.

23 The conversion catalyst preferably contains a Group VIII metal compound to have
24 sufficient activity for commercial use. By Group VIII metal compound as used herein is
25 meant the metal itself or a compound thereof. The Group VIII noble metals and their
26 compounds, platinum, palladium, and iridium, or combinations thereof can be used.
27 Rhenium or tin or a mixture thereof may also be used in conjunction with the Group VIII
28 metal compound and preferably a noble metal compound. The most preferred metal is
29 platinum. The amount of Group VIII metal present in the conversion catalyst should be
30 within the normal range of use in reforming catalysts, from about 0.05 to 2.0 weight percent,
31 preferably 0.2 to 0.8 weight percent.

32 It is critical to the selective production of aromatics in useful quantities that the

1 conversion catalyst be substantially free of acidity, for example, by neutralizing the zeolite
2 with a basic metal, e.g., alkali metal, compound. Methods for rendering the catalyst free of
3 acidity are known in the art. See the aforementioned U.S. Patent No. 4,910,006 and U.S.
4 Patent No. 5,316,753 for a description of such methods.

5 The preferred alkali metals are sodium, potassium, rubidium and cesium. The
6 zeolite itself can be substantially free of acidity only at very high silica:alumina mole ratios.

7 Catalytic Cracking

8 Hydrocarbon cracking stocks can be catalytically cracked in the absence of hydrogen
9 using CIT-5, preferably predominantly in the hydrogen form.

10 When CIT-5 is used as a catalytic cracking catalyst in the absence of hydrogen, the
11 catalyst may be employed in conjunction with traditional cracking catalysts, e.g., any
12 aluminosilicate heretofore employed as a component in cracking catalysts. Typically, these
13 are large pore, crystalline aluminosilicates. Examples of these traditional cracking catalysts
14 are disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent
15 No 5,316,753. When a traditional cracking catalyst (TC) component is employed, the
16 relative weight ratio of the TC to the CIT-5 is generally between about 1:10 and about
17 500:1, desirably between about 1:10 and about 200:1, preferably between about 1:2 and
18 about 50:1, and most preferably is between about 1:1 and about 20:1. The novel zeolite
19 and/or the traditional cracking component may be further ion exchanged with rare earth ions
20 to modify selectivity.

21 The cracking catalysts are typically employed with an inorganic oxide matrix
22 component. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent
23 No. 5,316,753 for examples of such matrix components.

24 Isomerization

25 The present catalyst, preferably predominantly in the hydrogen form, is believed to
26 be active and selective for isomerizing C₄ to C₇ hydrocarbons. The activity means that the
27 catalyst can operate at relatively low temperature which thermodynamically favors highly
28 branched paraffins. Consequently, the catalyst can produce a high octane product. The
29 selectivity means that a relatively high liquid yield can be achieved when the catalyst is run
30 at a high octane.

31 The present process comprises contacting the isomerization catalyst, i.e., a catalyst
32 comprising CIT-5 in the hydrogen form, with a hydrocarbon feed under isomerization

1 conditions. The feed is preferably a light straight run fraction, boiling within the range of
2 30°F to 250°F and preferably from 60°F to 200°F. Preferably, the hydrocarbon feed for the
3 process comprises a substantial amount of C₄ to C₇ normal and slightly branched low octane
4 hydrocarbons, more preferably C₅ and C₆ hydrocarbons.

5 It is preferable to carry out the isomerization reaction in the presence of hydrogen.
6 Preferably, hydrogen is added to give a hydrogen to hydrocarbon ratio (H₂/HC) of between
7 0.5 and 10 H₂/HC, more preferably between 1 and 8 H₂/HC. See the aforementioned U.S.
8 Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a further discussion of
9 isomerization process conditions.

10 A low sulfur feed is especially preferred in the present process. The feed preferably
11 contains less than 10 ppm, more preferably less than 1 ppm, and most preferably less than
12 0.1 ppm sulfur. In the case of a feed which is not already low in sulfur, acceptable levels
13 can be reached by hydrogenating the feed in a presaturation zone with a hydrogenating
14 catalyst which is resistant to sulfur poisoning. See the aforementioned U.S. Patent
15 No. 4,910,006 and U.S. Patent No. 5,316,753 for a further discussion of this
16 hydrodesulfurization process.

17 It is preferable to limit the nitrogen level and the water content of the feed. Catalysts
18 and processes which are suitable for these purposes are known to those skilled in the art.

19 After a period of operation, the catalyst can become deactivated by sulfur or coke.
20 See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a
21 further discussion of methods of removing this sulfur and coke, and of regenerating the
22 catalyst.

23 The conversion catalyst preferably contains a Group VIII metal compound to have
24 sufficient activity for commercial use. By Group VIII metal compound as used herein is
25 meant the metal itself or a compound thereof. The Group VIII noble metals and their
26 compounds, platinum, palladium, and iridium, or combinations thereof can be used.
27 Rhenium and tin may also be used in conjunction with the noble metal. The most preferred
28 metal is platinum. The amount of Group VIII metal present in the conversion catalyst
29 should be within the normal range of use in isomerizing catalysts, from about 0.05 to
30 2.0 weight percent, preferably 0.2 to 0.8 weight percent.

Alkylation and Transalkylation

32 CIT-5 can be used in a process for the alkylation or transalkylation of an aromatic

1 hydrocarbon. The process comprises contacting the aromatic hydrocarbon with a C₂ to C₁₆
2 olefin alkylating agent or a polyalkyl aromatic hydrocarbon transalkylating agent, under at
3 least partial liquid phase conditions, and in the presence of a catalyst comprising CIT-5.

4 CIT-5 can also be used for removing benzene from gasoline by alkylating the
5 benzene as described above and removing the alkylated product from the gasoline.

6 For high catalytic activity, the CIT-5 zeolite should be predominantly in its hydrogen
7 ion form. It is preferred that, after calcination, at least 80% of the cation sites are occupied
8 by hydrogen ions and/or rare earth ions.

9 Examples of suitable aromatic hydrocarbon feedstocks which may be alkylated or
10 transalkylated by the process of the invention include aromatic compounds such as benzene,
11 toluene and xylene. The preferred aromatic hydrocarbon is benzene. There may be
12 occasions where naphthalene derivatives may be desirable. Mixtures of aromatic
13 hydrocarbons may also be employed.

14 Suitable olefins for the alkylation of the aromatic hydrocarbon are those containing 2
15 to 20, preferably 2 to 4, carbon atoms, such as ethylene, propylene, butene-1, trans-butene-2
16 and cis-butene-2, or mixtures thereof. There may be instances where pentenes are desirable.
17 The preferred olefins are ethylene and propylene. Longer chain alpha olefins may be used as
18 well.

19 When transalkylation is desired, the transalkylating agent is a polyalkyl aromatic
20 hydrocarbon containing two or more alkyl groups that each may have from 2 to about
21 4 carbon atoms. For example, suitable polyalkyl aromatic hydrocarbons include di-, tri- and
22 tetra-alkyl aromatic hydrocarbons, such as diethylbenzene, triethylbenzene,
23 diethylmethylbenzene (diethyltoluene), di-isopropylbenzene, di-isopropyltoluene,
24 dibutylbenzene, and the like. Preferred polyalkyl aromatic hydrocarbons are the dialkyl
25 benzenes. A particularly preferred polyalkyl aromatic hydrocarbon is di-isopropylbenzene.

26 When alkylation is the process conducted, reaction conditions are as follows. The
27 aromatic hydrocarbon feed should be present in stoichiometric excess. It is preferred that
28 molar ratio of aromatics to olefins be greater than four-to-one to prevent rapid catalyst
29 fouling. The reaction temperature may range from 100°F to 600°F, preferably 250°F to
30 450°F. The reaction pressure should be sufficient to maintain at least a partial liquid phase
31 in order to retard catalyst fouling. This is typically 50 psig to 1000 psig depending on the
32 feedstock and reaction temperature. Contact time may range from 10 seconds to 10 hours,

1 but is usually from 5 minutes to an hour. The weight hourly space velocity (WHSV), in
2 terms of grams (pounds) of aromatic hydrocarbon and olefin per gram (pound) of catalyst
3 per hour, is generally within the range of about 0.5 to 50.

4 When transalkylation is the process conducted, the molar ratio of aromatic
5 hydrocarbon will generally range from about 1:1 to 25:1, and preferably from about 2:1 to
6 20:1. The reaction temperature may range from about 100°F to 600°F, but it is preferably
7 about 250°F to 450°F. The reaction pressure should be sufficient to maintain at least a
8 partial liquid phase, typically in the range of about 50 psig to 1000 psig, preferably 300 psig
9 to 600 psig. The weight hourly space velocity will range from about 0.1 to 10. U.S. Patent
10 No. 5,082,990 issued on January 21, 1992 to Hsieh, et al. describes such processes and is
11 incorporated herein by reference.

12 Isomerization of Olefins

13 CIT-5 can be used to isomerize olefins. The feed stream is a hydrocarbon stream
14 containing at least one C₄-₆ olefin, preferably a C₄-₆ normal olefin, more preferably normal
15 butene. Normal butene as used in this specification means all forms of normal butene, e.g.,
16 1-butene, cis-2-butene, and trans-2-butene. Typically, hydrocarbons other than normal
17 butene or other C₄-₆ normal olefins will be present in the feed stream. These other
18 hydrocarbons may include, e.g., alkanes, other olefins, aromatics, hydrogen, and inert gases.

19 The feed stream typically may be the effluent from a fluid catalytic cracking unit or a
20 methyl-tert-butyl ether unit. A fluid catalytic cracking unit effluent typically contains about
21 40-60 weight percent normal butenes. A methyl-tert-butyl ether unit effluent typically
22 contains 40-100 weight percent normal butene. The feed stream preferably contains at least
23 about 40 weight percent normal butene, more preferably at least about 65 weight percent
24 normal butene. The terms iso-olefin and methyl branched iso-olefin may be used
25 interchangeably in this specification.

26 The process is carried out under isomerization conditions. The hydrocarbon feed is
27 contacted in a vapor phase with a catalyst comprising the CIT-5. The process may be
28 carried out generally at a temperature from about 625°F to about 950°F (329-510°C), for
29 butenes, preferably from about 700°F to about 900°F (371-482°C), and about 350°F to
30 about 650°F (177-343°C) for pentenes and hexenes. The pressure ranges from
31 subatmospheric to about 200 psig, preferably from about 15 psig to about 200 psig, and
32 more preferably from about 1 psig to about 150 psig.

1 The liquid hourly space velocity during contacting is generally from about 0.1 to
2 about 50 hr⁻¹, based on the hydrocarbon feed, preferably from about 0.1 to about 20 hr⁻¹,
3 more preferably from about 0.2 to about 10 hr⁻¹, most preferably from about 1 to about
4 5 hr⁻¹. A hydrogen/hydrocarbon molar ratio is maintained from about 0 to about 30 or
5 higher. The hydrogen can be added directly to the feed stream or directly to the
6 isomerization zone. The reaction is preferably substantially free of water, typically less than
7 about two weight percent based on the feed. The process can be carried out in a packed bed
8 reactor, a fixed bed, fluidized bed reactor, or a moving bed reactor. The bed of the catalyst
9 can move upward or downward. The mole percent conversion of, e.g., normal butene to
10 iso-butene is at least 10, preferably at least 25, and more preferably at least 35.

11 Conversion of Paraffins to Aromatics

12 CIT-5 can be used to convert light gas C₂-C₆ paraffins to higher molecular weight
13 hydrocarbons including aromatic compounds. Preferably, the zeolite will contain a catalyst
14 metal or metal oxide wherein said metal is selected from the group consisting of Groups IB,
15 IIB, VIII and IIIA of the Periodic Table. Preferably, the metal is gallium, niobium, indium
16 or zinc in the range of from about 0.05 to 5% by weight.

17 Xylene Isomerization

18 CIT-5 may also be useful in a process for isomerizing one or more xylene isomers in
19 a C₈ aromatic feed to obtain ortho-, meta-, and para-xylene in a ratio approaching the
20 equilibrium value. In particular, xylene isomerization is used in conjunction with a separate
21 process to manufacture para-xylene. For example, a portion of the para-xylene in a mixed
22 C₈ aromatics stream may be recovered by crystallization and centrifugation. The mother
23 liquor from the crystallizer is then reacted under xylene isomerization conditions to restore
24 ortho-, meta- and para-xylenes to a near equilibrium ratio. At the same time, part of the
25 ethylbenzene in the mother liquor is converted to xylenes or to products which are easily
26 separated by filtration. The isomerate is blended with fresh feed and the combined stream is
27 distilled to remove heavy and light by-products. The resultant C₈ aromatics stream is then
28 sent to the crystallizer to repeat the cycle.

29 Optionally, isomerization in the vapor phase is conducted in the presence of 3.0 to
30 30.0 moles of hydrogen per mole of alkylbenzene (e.g., ethylbenzene). If hydrogen is used,
31 the catalyst should comprise about 0.1 to 2.0 wt% of a hydrogenation/dehydrogenation
32 component selected from Group VIII (of the Periodic Table) metal component, especially

1 platinum or nickel. By Group VIII metal component is meant the metals and their
2 compounds such as oxides and sulfides.

3 Optionally, the isomerization feed may contain 10 to 90 wt% of a diluent such as
4 toluene, trimethylbenzene, naphthenes or paraffins.

5 Oligomerization

6 It is expected that CIT-5 can also be used to oligomerize straight and branched chain
7 olefins having from about 2 to 21 and preferably 2-5 carbon atoms. The oligomers which
8 are the products of the process are medium to heavy olefins which are useful for both fuels,
9 i.e., gasoline or a gasoline blending stock and chemicals.

10 The oligomerization process comprises contacting the olefin feedstock in the
11 gaseous or liquid phase with a catalyst comprising CIT-5.

12 The zeolite can have the original cations associated therewith replaced by a wide
13 variety of other cations according to techniques well known in the art. Typical cations
14 would include hydrogen, ammonium and metal cations including mixtures of the same. Of
15 the replacing metallic cations, particular preference is given to cations of metals such as rare
16 earth metals, manganese, calcium, as well as metals of Group II of the Periodic Table, e.g.,
17 zinc, and Group VIII of the Periodic Table, e.g., nickel. One of the prime requisites is that
18 the zeolite have a fairly low aromatization activity, i.e., in which the amount of aromatics
19 produced is not more than about 20% by weight. This is accomplished by using a zeolite
20 with controlled acid activity [alpha value] of from about 0.1 to about 120, preferably from
21 about 0.1 to about 100, as measured by its ability to crack n-hexane.

22 Alpha values are defined by a standard test known in the art, e.g., as shown in U.S.
23 Patent No. 3,960,978 issued on June 1, 1976 to Givens et al. which is incorporated totally
24 herein by reference. If required, such zeolites may be obtained by steaming, by use in a
25 conversion process or by any other method which may occur to one skilled in this art.

26 Condensation of Alcohols

27 CIT-5 can be used to condense lower aliphatic alcohols having 1 to 10 carbon atoms
28 to a gasoline boiling point hydrocarbon product comprising mixed aliphatic and aromatic
29 hydrocarbon. The process disclosed in U.S. Patent No. 3,894,107, issued July 8, 1975 to
30 Butter et al., describes the process conditions used in this process, which patent is
31 incorporated totally herein by reference.

32 The catalyst may be in the hydrogen form or may be base exchanged or impregnated

1 to contain ammonium or a metal cation complement, preferably in the range of from about
2 0.05 to 5% by weight. The metal cations that may be present include any of the metals of
3 the Groups I through VIII of the Periodic Table. However, in the case of Group IA metals,
4 the cation content should in no case be so large as to effectively deactivate the catalyst, nor
5 should the exchange be such as to eliminate all acidity. There may be other processes
6 involving treatment of oxygenated substrates where a basic catalyst is desired.

7 Other Uses for CIT-5

8 CIT-5 can also be used as an adsorbent with high selectivities based on molecular
9 sieve behavior and also based upon preferential hydrocarbon packing within the pores.

10 CIT-5 may also be used for the catalytic reduction of the oxides of nitrogen in a gas
11 stream. Typically, the gas stream also contains oxygen, often a stoichiometric excess
12 thereof. Also, the CIT-5 may contain a metal or metal ions within or on it which are capable
13 of catalyzing the reduction of the nitrogen oxides. Examples of such metals or metal ions
14 include copper, cobalt and mixtures thereof.

15 One example of such a process for the catalytic reduction of oxides of nitrogen in the
16 presence of a zeolite is disclosed in U.S. Patent No. 4,297,328, issued October 27, 1981 to
17 Ritscher et al., which is incorporated by reference herein. There, the catalytic process is the
18 combustion of carbon monoxide and hydrocarbons and the catalytic reduction of the oxides
19 of nitrogen contained in a gas stream, such as the exhaust gas from an internal combustion
20 engine. The zeolite used is metal ion-exchanged, doped or loaded sufficiently so as to
21 provide an effective amount of catalytic copper metal or copper ions within or on the zeolite.
22 In addition, the process is conducted in an excess of oxidant, e.g., oxygen.

23 EXAMPLES

24 The following examples demonstrate but do not limit the present invention.

25 Example 1

26 Synthesis of N(16) methylsparteinium hydroxide (MeSPA OH)

27 21.1 Grams (50 mmol) of (-) sparteine sulfate pentahydrate (Aldrich) is added to 50 ml of a
28 3 M NaOH solution. The resulting suspension is stirred until the crystals are completely
29 dissolved and two phases form. The organic phase is extracted three times with 25 ml
30 portions of diethyl ether and the combined extracts are dried over solid KOH (85%) and
31 filtered. The solvent is then evaporated at room temperature under vacuum. The recovered
32 (-) sparteine is dissolved in 100 ml of acetone containing 28.3 g (1.5 equiv.) of methyl
33 iodide. The resulting reaction mixture is stirred in the dark for 24 hours. and the yellow

1 solid product which forms is filtered after the addition of 50 ml of diethyl ether. The
 2 recovered solid (15.2 g, 81% yield) is recrystallized twice in 2-propanol by adding ethyl
 3 acetate until turbidity to give 13.7 g (73% yield) of slightly yellow crystals. Analyses:
 4 Calculated for $C_{16}N_2H_{29}I$: C, 51.1%; N, 7.4%; H, 7.7%; I, 33.8%. Found: C, 51.0%; N,
 5 7.4%; H, 7.9%; I, 33.7%. The IR spectrum of the product agrees with a previously reported
 6 spectrum for N(16) methylsparteinium iodide.

7 Amberlite IRA-400(Cl) (Aldrich) anion exchange resin, exchanged to the bromide
8 form, is used to convert the iodide salt prepared as above to the corresponding bromide.
9 Typically, 7.52 g of N(16) methylsparteinium iodide (20 mmol) is dissolved in 50 ml of
10 water and exchanged in an ion exchange column containing 100 ml of anion exchange resin
11 (with 140 mmol of exchange capacity). After washing the column with an additional 200 ml
12 of distilled water, the aqueous solution obtained is evaporated in a rotavapor until dryness
13 and recrystallized as described above from 2-propanol-ethyl acetate. Elemental analyses
14 indicate a yield of 95% for the bromide form. Similarly, the hydroxide form is obtained
15 using Amberlite IRA-400 (OH) anion exchange resin. After exchange, the aqueous solution
16 is concentrated to 50 ml. The yield is 92.8% based on titration of the resultant solution and
17 gives a concentration of 0.371 M of N(16) methylsparteinium hydroxide.

Example 2

Preparation of Silicate CIT-5

0.018 Gram of LiOH anhydrous powder is dissolved in 2.54 g of distilled water. To the resulting solution is added 2.21 g of N(16) methylsparteinium hydroxide (MeSPA OH) solution (18.2 wt%) and the resulting reaction mixture is stirred for 10 minutes. SiO₂ (Ludox HS-30 from E. I. duPont), 1.5 g, is added to the reaction mixture and the mixture is stirred for two hours. The resulting gel is divided into portions and heated in three quartz tubes at 175°C for 7 days, 10 days and 11 days at autogenous pressure. The product is recovered by vacuum filtration and determined by X-ray diffraction (XRD) to be CIT-5 (the product recovered after 10 days also contains some amorphous material).

28 Typical XRD lines for the as-made (i.e., uncalcined) product of this example is
29 indicated in Table III below.

1

TABLE III

| <u>2 Theta</u> | <u>d</u> | <u>I/I₀ x 100</u> |
|----------------|----------|------------------------------|
| 6.957 | 12.695 | 77 |
| 7.288 | 12.119 | 50 |
| 12.810 | 6.905 | 4 |
| 13.929 | 6.353 | 37 |
| 17.093 | 5.183 | 3 |
| 18.963 | 4.676 | 100 |
| 19.588 | 4.529 | 25 |
| 20.001 | 4.436 | 57 |
| 20.499 | 4.329 | 40 |
| 20.953 | 4.236 | 60 |
| 21.770 | 4.079 | 3 |
| 21.931 | 4.050 | 8 |
| 22.613 | 3.929 | 7 |
| 23.410 | 3.797 | 13 |
| 24.218 | 3.672 | 6 |
| 24.625 | 3.612 | 34 |
| 25.796 | 3.451 | 5 |
| 26.097 | 3.412 | 7 |
| 26.733 | 3.332 | 59 |
| 27.116 | 3.286 | 18 |
| 28.224 | 3.159 | 28 |
| 29.378 | 3.038 | 4 |
| 29.818 | 2.994 | 6 |
| 31.374 | 2.849 | 11 |
| 31.550 | 2.833 | 4 |

| | | |
|--------|-------|----|
| 32.990 | 2.713 | 6 |
| 33.980 | 2.636 | 5 |
| 35.330 | 2.539 | 4 |
| 35.636 | 2.517 | 10 |
| 36.417 | 2.465 | 7 |
| 37.027 | 2.426 | 5 |
| 37.700 | 2.384 | 4 |
| 38.731 | 2.323 | 4 |
| 44.699 | 2.026 | 11 |
| 49.424 | 1.843 | 4 |

Example 3

Synthesis of CIT-5 in the Presence of Zinc

3 In a manner similar to that described in Example 2, CIT-5 is made from the
4 following components:

5 0.012 g LiOH

6 1.70 g distilled water

7 1.47 g MeSPA OH solution (18.2 wt%)

8 0.043 g $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$

9 1.0 g SiO_2 (Ludox HS-30)

10 This produces a gel composition, in terms of mole ratios, as follows:

11 0.1 LiOH : 0.04 Zn(CH₃COO)₂·2H₂O : 0.2 MeSPA OH : SiO₂ : 40 H₂O

12 Product is recovered by vacuum filtration after 13 days and 15 days, and determined
13 by XRD to be CIT-5 (the product recovered after 15 days also contains some unknown
14 material).

15 Typical XRD lines for the as-made product of this example is indicated in Table IV
16 below.

1

TABLE IV

| <u>2 Theta</u> | <u>d</u> | <u>I/I₀ x 100</u> |
|----------------|----------|------------------------------|
| 6.903 | 12.794 | 17 |
| 7.268 | 12.152 | 43 |
| 12.001 | 7.368 | 7 |
| 12.846 | 6.886 | 5 |
| 13.841 | 6.393 | 9 |
| 14.597 | 6.064 | 3 |
| 16.331 | 5.423 | 34 |
| 18.930 | 4.684 | 61 |
| 19.641 | 4.516 | 40 |
| 19.967 | 4.443 | 58 |
| 20.432 | 4.343 | 40 |
| 20.826 | 4.262 | 21 |
| 21.590 | 4.113 | 30 |
| 21.963 | 4.044 | 18 |
| 23.348 | 3.807 | 8 |
| 24.208 | 3.674 | 3 |
| 24.548 | 3.623 | 20 |
| 25.878 | 3.440 | 11 |
| 26.799 | 3.324 | 100 |
| 27.146 | 3.282 | 23 |
| 28.129 | 3.170 | 25 |
| 29.964 | 2.990 | 3 |
| 30.209 | 2.958 | 2 |
| 31.276 | 2.858 | 6 |
| 31.625 | 2.827 | 3 |

| | | |
|--------|-------|----|
| 32.913 | 2.719 | 4 |
| 33.462 | 2.676 | 5 |
| 33.719 | 2.656 | 4 |
| 35.569 | 2.522 | 20 |
| 36.265 | 2.475 | 8 |
| 37.051 | 2.424 | 6 |
| 37.848 | 2.375 | 5 |
| 38.646 | 2.328 | 3 |
| 44.625 | 2.029 | 4 |
| 44.828 | 2.020 | 6 |
| 47.102 | 1.928 | 4 |
| 49.616 | 1.836 | 5 |

1 After the product is calcined, it has the XRD lines indicated in Table V below.

2

TABLE V

| <u>2 Theta</u> | <u>d</u> | <u>I/I₀ x 100</u> |
|----------------|----------|------------------------------|
| 6.913 | 12.777 | 39 |
| 7.305 | 12.092 | 100 |
| 12.224 | 7.235 | 7 |
| 12.921 | 6.846 | 13 |
| 13.830 | 6.398 | - |
| 13.917 | 6.358 | - |
| 18.995 | 4.668 | 41 |
| 19.754 | 4.491 | 21 |
| 20.044 | 4.426 | 60 |
| 20.503 | 4.328 | 47 |
| 20.864 | 4.254 | 17 |
| 21.295 | 4.169 | 10 |

| | | |
|--------|-------|----|
| 21.645 | 4.102 | 28 |
| 22.103 | 4.018 | 10 |
| 22.568 | 3.937 | 2 |
| 23.409 | 3.797 | 6 |
| 24.319 | 3.657 | 7 |
| 24.612 | 3.614 | 13 |
| 26.016 | 3.422 | 7 |
| 26.172 | 3.402 | 3 |
| 26.944 | 3.306 | 57 |
| 27.282 | 3.266 | 16 |
| 28.059 | 3.178 | 6 |
| 28.222 | 3.160 | 18 |
| 29.910 | 2.985 | 3 |
| 30.254 | 2.952 | 1 |
| 31.393 | 2.847 | 5 |
| 31.778 | 2.814 | 1 |
| 33.020 | 2.710 | 4 |
| 33.589 | 2.666 | 2 |
| 33.876 | 2.644 | 0 |
| 34.358 | 2.608 | 1 |
| 35.702 | 2.513 | 21 |
| 36.289 | 2.474 | 3 |
| 36.427 | 2.465 | 6 |
| 37.233 | 2.413 | 5 |
| 38.024 | 2.365 | 3 |
| 38.807 | 2.319 | 1 |
| 43.680 | 2.070 | 2 |

| | | |
|--------|-------|---|
| 44.596 | 2.030 | 1 |
| 45.017 | 2.012 | 4 |
| 45.921 | 1.975 | 1 |
| 47.293 | 1.921 | 3 |
| 48.250 | 1.885 | 0 |
| 48.846 | 1.863 | 0 |
| 49.869 | 1.827 | 3 |
| 50.537 | 1.805 | 3 |

Example 4

Synthesis of Aluminosilicate CIT-5

In a manner similar to that described in Example 2, aluminosilicate CIT-5 is made from the following components:

5 0.018 g LiOH

6 3.47 g distilled water

7 1.27 g MeSPA OH solution (31.0 wt%)

8 0.028 g Al(NO₃)₃·9H₂O

9 1.50 g SiO_2 (Ludox HS-30)

10 This produces a gel composition, in terms of mole ratios, as follows:

0.1 LiOH : 0.01 Al(NO₃)₃·9H₂O : 0.2 MeSPAOH : SiO₂ : 40 H₂O

Product is recovered by vacuum filtration after 7 days and 9 days, and determined by

13 XRD to be GIT-5.

14 Typical XRD lines for the as-made product of this example is indicated in Table VI
15 below.

1

TABLE VI

| <u>2 Theta</u> | <u>d</u> | <u>IL₀ x 100</u> |
|----------------|----------|-----------------------------|
| 6.334 | 13.942 | 3 |
| 7.000 | 12.617 | 100 |
| 7.287 | 12.122 | 25 |
| 12.650 | 6.992 | 2 |
| 12.825 | 6.897 | 3 |
| 13.010 | 6.799 | 2 |
| 13.361 | 6.621 | 2 |
| 13.972 | 6.333 | 58 |
| 14.590 | 6.066 | 3 |
| 18.170 | 4.878 | 3 |
| 18.323 | 4.838 | 3 |
| 18.992 | 4.669 | 73 |
| 19.599 | 4.526 | 18 |
| 20.032 | 4.429 | 41 |
| 20.523 | 4.324 | 31 |
| 20.996 | 4.228 | 99 |
| 21.800 | 4.074 | 3 |
| 21.981 | 4.041 | 6 |
| 23.447 | 3.791 | 9 |
| 24.251 | 3.667 | 5 |
| 24.655 | 3.608 | 31 |
| 25.393 | 3.505 | 4 |
| 25.802 | 3.450 | 3 |
| 26.104 | 3.411 | 4 |
| 26.749 | 3.330 | 45 |

| | | |
|--------|-------|----|
| 27.148 | 3.282 | 13 |
| 28.130 | 3.170 | 22 |
| 28.234 | 3.158 | 23 |
| 29.836 | 2.992 | 3 |
| 31.374 | 2.849 | 8 |
| 33.065 | 2.707 | 4 |
| 33.481 | 2.674 | 4 |
| 35.308 | 2.540 | 3 |
| 35.675 | 2.515 | 8 |
| 36.492 | 2.460 | 7 |
| 37.007 | 2.427 | 4 |
| 37.744 | 2.382 | 4 |
| 38.796 | 2.319 | 3 |
| 44.750 | 2.024 | 9 |
| 47.198 | 1.924 | 3 |
| 49.639 | 1.835 | 2 |

1 After the product is calcined, it has the XRD lines indicated in Table VII below.

2

TABLE VII

| <u>2 Theta</u> | <u>d</u> | <u>I/I₀ x 100</u> |
|----------------|----------|------------------------------|
| 6.922 | 12.760 | 100 |
| 7.301 | 12.098 | 86 |
| 12.235 | 7.228 | 11 |
| 12.920 | 6.847 | 6 |
| 13.869 | 6.380 | 7 |
| 17.105 | 5.180 | - |
| 17.161 | 5.163 | 1 |
| 18.515 | 4.788 | 1 |

| | | |
|--------|-------|----|
| 18.989 | 4.670 | 40 |
| 19.730 | 4.496 | 11 |
| 20.041 | 4.427 | 31 |
| 20.510 | 4.327 | 26 |
| 20.876 | 4.252 | 26 |
| 23.437 | 3.793 | 5 |
| 24.301 | 3.660 | 4 |
| 24.613 | 3.614 | 18 |
| 25.235 | 3.526 | 2 |
| 26.008 | 3.423 | 3 |
| 26.147 | 3.405 | 4 |
| 26.923 | 3.309 | 29 |
| 27.268 | 3.268 | 8 |
| 27.947 | 3.190 | 4 |
| 28.222 | 3.160 | 16 |
| 29.887 | 2.987 | 1 |
| 30.223 | 2.955 | 1 |
| 31.367 | 2.850 | 5 |
| 31.796 | 2.812 | 1 |
| 32.232 | 2.775 | 1 |
| 33.010 | 2.711 | 3 |
| 33.563 | 2.668 | 2 |
| 33.849 | 2.646 | 1 |
| 34.345 | 2.609 | 1 |
| 35.152 | 2.551 | - |
| 35.690 | 2.514 | 7 |
| 36.337 | 2.470 | 4 |

| | | |
|--------|-------|---|
| 37.208 | 2.415 | 3 |
| 37.591 | 2.391 | 1 |
| 38.018 | 2.365 | 2 |
| 38.757 | 2.322 | 1 |
| 39.350 | 2.288 | - |
| 40.031 | 2.251 | - |
| 40.782 | 2.211 | - |
| 41.103 | 2.194 | - |
| 41.957 | 2.152 | - |
| 42.892 | 2.107 | 1 |
| 43.694 | 2.070 | 1 |
| 44.581 | 2.031 | 2 |
| 44.997 | 2.013 | 2 |
| 45.937 | 1.974 | 1 |
| 47.281 | 1.921 | 2 |
| 48.265 | 1.884 | - |
| 48.863 | 1.862 | - |
| 49.857 | 1.828 | 2 |
| 50.562 | 1.804 | 3 |

Example 5

Synthesis of Aluminosilicate CIT-5

In a manner similar to that described in Example 2, aluminosilicate CIT-5 is made from the following components:

- 5 0.18g LiOH
- 6 3.47g distilled water
- 7 1.27g MeSPA OH solution (31.0 wt%)
- 8 0.048g Al(NO₃)₃·9H₂O
- 9 1.5g SiO₂ (Ludox HS-30)

10 This produces a gel composition, in terms of mole ratios, as follows:

11 0.1 LiOH : 0.02 Al(NO₃)₃ : 0.2 MeSPA OH : SiO₂ : 40 H₂O

1 Product is recovered after 21 days and determined by XRD to be a mixture of
2 amorphous material and CIT-5.

3 Comparative Example A

4 Attempted Synthesis of Aluminosilicate CIT-5

5 In a manner similar to that described in Example 2, aluminosilicate CIT-5 is made
6 from the following components:

7 0.18g LiOH
8 3.35g distilled water
9 1.27g MeSPAOH solution (31.0 wt%)
10 0.281g Al(NO₃)₃·9H₂O
11 1.5g SiO₂ (Ludox HS-30)

12 This produces a gel composition, in terms of mole ratios, as follows:

13 0.1 LiOH : 0.1 Al(NO₃)₃ : 0.2 MeSPAOH : SiO₂ : 40 H₂O

14 Product is recovered after 60 days and determined by XRD to be amorphous material.

15 Example 6

16 Synthesis of Borosilicate CIT-5

17 In a manner similar to that described in Example 2, borosilicate CIT-5 is made from
18 the following components:

19 0.18g LiOH
20 3.47g distilled water
21 1.27g MeSPAOH solution (31.0 wt%)
22 0.0046g H₃BO₃
23 1.5g SiO₂ (Ludox HS-30)

24 This produces a gel composition, in terms of mole ratios, as follows:

25 0.1 LiOH : 0.01 H₃BO₃ : 0.2 MeSPAOH : SiO₂ : 40 H₂O

26 Product is recovered after 7 days and determined by XRD to be CIT-5.

27 Example 7

28 Synthesis of Gallosilicate CIT-5

29 In a manner similar to that described in Example 2, gallosilicate CIT-5 is made from
30 the following components:

31 0.18g LiOH
32 3.47g distilled water
33 1.27g MeSPAOH solution (31.0 wt%)
34 0.019g Ga(NO₃)₃·xH₂O (x=3.4)
35 1.5g SiO₂ (Ludox HS-30)

36 This produces a gel composition, in terms of mole ratios, as follows:

1 0.1 LiOH : 0.01 Ga(NO₃)₃ : 0.2 MeSPA OH : SiO₂ : 40 H₂O

2 Product is recovered after 7 days and determined by XRD to be CIT-5.

3 Example 8

4 Synthesis of Silicate CIT-5

5 In a manner similar to that described in Example 2, silicate CIT-5 is synthesized in a
6 Teflon lined autoclave instead of quartz tubes from the following components:

7 0.19g LiOH

8 4.22g distilled water

9 0.86g MeSPA OH solution (49.8 wt%)

10 1.6g SiO₂ (Ludox HS-30)

11 This produces a gel composition, in terms of mole ratios, as follows:

12 0.1 LiOH : 0.2 MeSPA OH : SiO₂ : 40 H₂O

13 Product is recovered after 6 days and determined by XRD to be CIT-5.

14 Example 9

15 Synthesis of Silicate CIT-5 Using Li and Na

16 In a manner similar to that described in Example 8, silicate CIT-5 is synthesized
17 from the following components:

18 0.14g LiOH

19 0.016g 50 wt% aqueous NaOH solution

20 4.22g distilled water

21 0.86g MeSPA OH solution (49.8 wt%)

22 1.6g SiO₂ (Ludox HS-30)

23 This produces a gel composition, in terms of mole ratios, as follows:

24 0.075 LiOH : 0.025 NaOH : 0.2 MeSPA OH : SiO₂ : 40 H₂O

25 Product is recovered after 5 days and determined by XRD to be CIT-5.

26 Example 10

27 Synthesis of Silicate CIT-5 Using Li and K

28 In a manner similar to that described in Example 8, silicate CIT-5 is synthesized
29 from the following components:

30 0.14g LiOH

31 0.022g 50 wt% aqueous KOH solution

32 4.22g distilled water

33 0.86g MeSPA OH solution (49.8 wt%)

34 1.6g SiO₂ (Ludox HS-30)

35 This produces a gel composition, in terms of mole ratios, as follows:

36 0.075 LiOH : 0.025 KOH : 0.2 MeSPA OH : SiO₂ : 40 H₂O

1 Product is recovered after 5 days and determined by XRD to be CIT-5 and amorphous
2 material.

3 Example 11

4 Synthesis of Aluminosilicate CIT-5

5 In the Teflon cup for a small Parr reactor is combined 3.4 grams of a 0.66 M solution
6 of MeSPA OH template with 8.5 grams of water and 0.06 gram of lithium carbonate. 0.90
7 Gram of 390-HUA Y zeolite (sold by Tosoh) is added as a source of both silicon and
8 aluminum. The reactor is sealed and heated at 160°C while being tumbled at 43 RPM for a
9 period of 12 days. Upon cooling the reactor, the solid product is collected by filtration,
10 washed and dried. The product is determined by XRD to be CIT-5.

11 The CIT-5 product is calcined and ammonium ion exchanged as previously
12 described.

13 Example 12

14 Preparation of Pd CIT-5

15 0.99 Gram of the ammonium exchanged CIT-5 prepared in Example 11 is slurried
16 into 9 ml of water and 2 ml of a 0.156 N ammonium hydroxide solution. A solution of
17 palladium tetraamine dinitrate buffered in ammonium hydroxide is then added. The
18 quantity of palladium is sufficient to provide 0.50 wt% Pd on the CIT-5 if completely ion
19 exchanged onto the zeolite. The zeolite and solution are allowed to stand for several days at
20 room temperature, after which the zeolite is filtered and washed. This product is then
21 calcined at 482°C after a slow ramp to 120°C followed by a 1 degree C/minute increase to
22 482°C. The zeolite is held at 482°C for three hours.

23 Example 13

24 Hydrocracking and Hydroisomerization of n-Hexadecane

25 Using Pd CIT-5

26 0.50 Gram of the Pd CIT-5 prepared in Example 12 is pressed into a tablet at 3000
27 psi, fractured, meshed to 20-40, and loaded into a stainless steel reactor. The zeolite is dried
28 in situ and the reactor temperature is brought to 600°F (315°C) and pressurized to 1200 psi
29 hydrogen flow. A n-hexadecane feed is introduced at 1.00 microliter/minute. At 167 hours
30 on stream and at 660°F (349°C), the catalyst is achieving 96% conversion. The liquid to gas
31 ratio of the converted products is 5.3. Iso/normal ratios for the gasoline fractions and
32 hexadecane are given below.

| Carbon No. | Iso/Normal ratio |
|------------|------------------|
| 4 | 1.95 |
| 5 | 3.19 |
| 6 | 2.89 |

1 M/YO₂ ≤ 0.05

3

4 wherein Y is silicon, germanium or a mixture thereof; W is aluminum, boron, gallium,
5 iron or mixtures thereof; a= 1 or 2, b=2 when a=1 and b=3 when a= 2 ; M is an alkali
6 metal; and Q comprises a N(16) methylsparteinium cation.

7

8 10. A zeolite according to claim 8 wherein W is aluminum and Y is silicon.

9

10 . 11. A zeolite according to claim 8 wherein W is boron and Y is silicon.

11

12 12. A zeolite according to claim 8 wherein W is gallium and Y is silicon.

13

14 13. A zeolite having a composition, as synthesized and in the anhydrous state, in terms of
15 mole ratios as follows:

16 YO_2/TiO_2 > 40

17 M/YO₂ ≤ 0.05

18 Q/YO₂ ≤ 0.05

19

20 wherein Y is silicon, germanium or a mixture thereof; M is an alkali metal; and Q
21 comprises a N(16) methylsparteinium cation.

22

23 14. A method of preparing a crystalline material comprising an oxide of a tetravalent
24 element or mixture of oxides of tetravalent elements and, optionally, an oxide of a
25 trivalent element or mixtures of oxides of trivalent elements, said method comprising
26 contacting in admixture under crystallization conditions sources of said oxides, a
27 source of alkali metal and a templating agent comprising a N(16) methylsparteinium
28 cation.

20

30 15. The method according to claim 14 wherein the tetravalent element is selected from the
31 group consisting of silicon, germanium and combinations thereof.

3

- 1 16. The method according to claim 14 wherein the trivalent element is selected from the
- 2 group consisting of aluminum, boron, gallium, iron and mixtures thereof.
- 3
- 4 17. The method according to claim 14 wherein the tetravalent element is silicon and the
- 5 trivalent element is aluminum.
- 6
- 7 18. The method according to claim 14 wherein the tetravalent element is silicon and the
- 8 trivalent element is boron.
- 9
- 10 19. The method according to claim 14 wherein the tetravalent element is silicon and the
- 11 trivalent element is gallium.
- 12
- 13 20. The method according to claim 14 wherein the tetravalent element is silicon and the
- 14 trivalent element is iron.
- 15
- 16 21. The method of claim 14 wherein the crystalline material has, after calcination, the
- 17 X-ray diffraction lines of Table II.
- 18
- 19 22. The method of claim 14 wherein the source of the alkali metal contains no alkali metal
- 20 other than lithium.
- 21
- 22 23. The method of claim 14 wherein the source of alkali metal contains lithium and
- 23 another alkali metal.
- 24
- 25 24. The method of claim 14 wherein the admixture further comprises a source of zinc.
- 26
- 27 25. A process for converting hydrocarbons comprising contacting a hydrocarbonaceous
- 28 feed at hydrocarbon converting conditions with a catalyst comprising a zeolite
- 29 comprising an oxide of a tetravalent element or mixture of oxides of tetravalent
- 30 elements and an optional oxide of a trivalent element or mixtures of oxides of trivalent
- 31 elements and having, after calcination, the X-ray diffraction lines of Table II.
- 32

- 1 26. The process of claim 25 wherein the zeolite is predominantly in the hydrogen form.
- 2
- 3 27. The process of claim 25 wherein the zeolite is substantially free of acidity.
- 4
- 5 28. The process of claim 25 wherein the process is a hydrocracking process comprising
- 6 contacting the catalyst with a hydrocarbon feedstock under hydrocracking conditions.
- 7
- 8 29. The process of claim 28 wherein the zeolite is predominantly in the hydrogen form.
- 9
- 10 30. The process of claim 25 wherein the process is a dewaxing process comprising
- 11 contacting the catalyst with a hydrocarbon feedstock under dewaxing conditions.
- 12
- 13 31. The process of claim 30 wherein the zeolite is predominantly in the hydrogen form.
- 14
- 15 32. The process of claim 25 wherein the process is a process for improving the viscosity
- 16 index of a dewaxed product of waxy hydrocarbon feeds comprising contacting the
- 17 catalyst with a waxy hydrocarbon feed under isomerization dewaxing conditions.
- 18
- 19 33. The process of claim 32 wherein the zeolite is predominantly in the hydrogen form.
- 20
- 21 34. The process of claim 25 wherein the process is a process for producing a C₂₀₊ lube oil
- 22 from a C₂₀₊ olefin feed comprising isomerizing said olefin feed under isomerization
- 23 conditions over the catalyst.
- 24
- 25 35. The process of claim 34 wherein the zeolite is predominantly in the hydrogen form.
- 26
- 27 36. The process of claim 34 wherein the catalyst further comprises at least one Group VIII
- 28 metal.
- 29
- 30 37. The process of claim 25 wherein the process is a process for catalytically dewaxing a
- 31 hydrocarbon oil feedstock boiling above about 350°F and containing straight chain and
- 32 slightly branched chain hydrocarbons comprising contacting said hydrocarbon oil
- 33 feedstock in the presence of added hydrogen gas at a hydrogen pressure of about 15-

1 3000 psi under dewaxing conditions with the catalyst.

2

3 38. The process of claim 37 wherein the zeolite is predominantly in the hydrogen form.

4

5 39. The process of claim 37 wherein the catalyst further comprises at least one Group VIII

6 metal.

7

8 40. The process of claim 37 wherein said catalyst comprises a layered catalyst comprising

9 a first layer comprising the zeolite and at least one Group VIII metal, and a second

10 layer comprising an aluminosilicate zeolite which is more shape selective than the

11 zeolite of said first layer.

12

13 41. The process of claim 25 wherein the process is a process for preparing a lubricating oil

14 which comprises:

15

16 hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain an

17 effluent comprising a hydrocracked oil; and

18

19 catalytically dewaxing said effluent comprising hydrocracked oil at a temperature of at

20 least about 400°F and at a pressure of from about 15 psig to about 3000 psig in the

21 presence of added hydrogen gas with the catalyst.

22

23 42. The process of claim 41 wherein the zeolite is predominantly in the hydrogen form.

24

25 43. The process of claim 41 wherein the catalyst further comprises at least one Group VIII

26 metal.

27

28 44. The process of claim 25 wherein the process is a process for isomerization dewaxing a

29 raffinate comprising contacting said raffinate in the presence of added hydrogen under

30 isomerization dewaxing conditions with the catalyst.

31

32 45. The process of claim 44 wherein the zeolite is predominantly in the hydrogen form.

33

- 1 46. The process of claim 44 wherein the catalyst further comprises at least one Group VIII
- 2 metal.
- 3
- 4 47. The process of claim 44 wherein the raffinate is bright stock.
- 5
- 6 48. The process of claim 25 wherein the process is a process for increasing the octane of a
- 7 hydrocarbon feedstock to produce a product having an increased aromatics content
- 8 comprising contacting a hydrocarbonaceous feedstock which comprises normal and
- 9 slightly branched hydrocarbons having a boiling range above about 40°C and less than
- 10 about 200°C under aromatic conversion conditions with the catalyst.
- 11
- 12 49. The process of claim 48 wherein the zeolite is substantially free of acid.
- 13
- 14 50. The process of claim 48 wherein the zeolite contains a Group VIII metal component.
- 15
- 16 51. The process of claim 25 wherein the process is a catalytic cracking process comprising
- 17 contacting a hydrocarbon feedstock in a reaction zone under catalytic cracking
- 18 conditions in the absence of added hydrogen with the catalyst.
- 19
- 20 52. The process of claim 51 wherein the zeolite is predominantly in the hydrogen form.
- 21
- 22 53. The process of claim 51 wherein the catalyst additionally comprises a large pore
- 23 crystalline cracking component.
- 24
- 25 54. The process of claim 25 wherein the process is an isomerization process for
- 26 isomerizing C₄ to C₇ hydrocarbons, comprising contacting a feed having normal and
- 27 slightly branched C₄ to C₇ hydrocarbons under isomerizing conditions with the
- 28 catalyst.
- 29
- 30 55. The process of claim 54 wherein the zeolite is predominantly in the hydrogen form.
- 31
- 32 56. The process of claim 54 wherein the zeolite has been impregnated with at least one
- 33 Group VIII metal.

1

2 57. The process of claim 54 wherein the catalyst has been calcined in a steam/air mixture

3 at an elevated temperature after impregnation of the Group VIII metal.

4

5 58. The process of claim 56 wherein the Group VIII metal is platinum.

6

7 59. The process of claim 25 wherein the process is a process for alkylating an aromatic

8 hydrocarbon which comprises contacting under alkylation conditions at least a molar

9 excess of an aromatic hydrocarbon with a C₂ to C₂₀ olefin under at least partial liquid

10 phase conditions and in the presence of the catalyst.

11

12 60. The process of claim 59 wherein the zeolite is predominantly in the hydrogen form.

13

14 61. The process of claim 59 wherein the olefin is a C₂ to C₄ olefin.

15

16 62. The process of claim 61 wherein the aromatic hydrocarbon and olefin are present in a

17 molar ratio of about 4:1 to about 20:1, respectively.

18

19 63. The process of claim 61 wherein the aromatic hydrocarbon is selected from the group

20 consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.

21

22 64. The process of claim 25 wherein the process is a process for transalkylating an

23 aromatic hydrocarbon which comprises contacting under transalkylating conditions an

24 aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon under at least partial

25 liquid phase conditions and in the presence of the catalyst.

26

27 65. The process of claim 64 wherein the zeolite is predominantly in the hydrogen form.

28

29 66. The process of claim 64 wherein the aromatic hydrocarbon and the polyalkyl aromatic

30 hydrocarbon are present in a molar ratio of from about 1:1 to about 25:1, respectively.

31

32 67. The process of claim 64 wherein the aromatic hydrocarbon is selected from the group

33 consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.

34

35 68. The process of claim 64 wherein the polyalkyl aromatic hydrocarbon is a

36 dialkylbenzene.

1
2 69. The process of claim 25 wherein the process is a process to convert paraffins to
3 aromatics which comprises contacting paraffins under conditions which cause
4 paraffins to convert to aromatics with a catalyst comprising the zeolite and gallium,
5 zinc, or a compound of gallium or zinc.

6

7 70. The process of claim 25 wherein the process is a process for isomerizing olefins
8 comprising contacting said olefin under conditions which cause isomerization of the
9 olefin with the catalyst.

10

11 71. The process of claim 25 wherein the process is a process for isomerizing an
12 isomerization feed comprising an aromatic C₈ stream of xylene isomers or mixtures of
13 xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio of ortho-,
14 meta and para-xlenes is obtained, said process comprising contacting said feed under
15 isomerization conditions with the catalyst.

16

17 72. The process of claim 25 wherein the process is a process for oligomerizing olefins
18 comprising contacting an olefin feed under oligomerization conditions with the
19 catalyst.

20

21 73. A process for converting lower alcohols and other oxygenated hydrocarbons
22 comprising contacting said lower alcohol or other oxygenated hydrocarbon under
23 conditions to produce liquid products with a catalyst comprising a zeolite comprising
24 an oxide of a tetravalent element or mixture of oxides of tetravalent elements and,
25 optionally, an oxide of a trivalent element or mixtures of oxides of trivalent elements
26 and having, after calcination, the X-ray diffraction lines of Table II.

27

28 74. In a process for the reduction of oxides of nitrogen contained in a gas stream in the
29 presence of oxygen wherein said process comprises contacting the gas stream with a
30 zeolite, the improvement comprising using as the zeolite a zeolite comprising an oxide
31 of a tetravalent element or mixture of oxides of tetravalent elements and, optionally, an
32 oxide of a trivalent element or mixtures of oxides of trivalent elements and having,

1 after calcination, the X-ray diffraction lines of Table II.

2

3 75. The process of claim 74 wherein said zeolite contains a metal or metal ions capable of

4 catalyzing the reduction of the oxides of nitrogen.

5

6 76. The process of claim 75 wherein the metal is copper, cobalt or mixtures thereof.

7

8 77. The process of claim 75 wherein the gas stream is the exhaust stream of an internal

9 combustion engine.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/16401

A. CLASSIFICATION OF SUBJECT MATTER

| | | | | | |
|-------|------------|-----------|-----------|-----------|-----------|
| IPC 6 | C01B39/48 | C01B39/08 | C01B39/12 | C01B37/02 | B01J29/70 |
| | B01J29/86 | B01J29/87 | C10G45/64 | C10G65/04 | C10G65/12 |
| | C10G35/095 | C07C2/66 | C07C6/12 | C07C5/41 | C07C5/22 |

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|---|----------------------------------|
| P, X | PAUL WAGNER ET AL.: "CIT-5: a high-silica zeolite with 14-ring pores" CHEMICAL COMMUNICATIONS., no. 22, 21 November 1997, pages 2179-2180, XP002086050 CIETY OF CHEMISTRY GB see the whole document --- | 1-3, 7-10, 13-17, 21,22 |
| A | US 5 271 922 A (NAKAGAWA YUMI) 21 December 1993 see the whole document --- | 1-24 |
| A | US 4 936 977 A (ZONES STACEY I ET AL) 26 June 1990 see the whole document --- | 1-5, 7-12,25 |
| | | -/- |



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Date of the actual completion of the international search

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|----------|---|-----------------------|
| A | WO 95 22507 A (CHEVRON USA INC) 24 August 1995 see claims 1-47 see page 21 - page 35 | 1,25-73 |
| A | US 5 580 540 A (NAKAGAWA YUMI) 3 December 1996 see column 10, line 5 - column 18, line 31 | 1,25-77 |

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Information on patent family members

Inte ional Application No

PCT/US 98/16401

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
|--|------------------|---|--|--|
| US 5271922 | A 21-12-1993 | NONE | | |
| US 4936977 | A 26-06-1990 | AU 592617 B AU 6806087 A CA 1279058 A EP 0231019 A IN 169668 A JP 1825705 C JP 62191418 A US 4834958 A | | 18-01-1990 30-07-1987 15-01-1991 05-08-1987 30-11-1991 28-02-1994 21-08-1987 30-05-1989 |
| WO 9522507 | A 24-08-1995 | AU 1699495 A EP 0746529 A US 5653956 A US 5685973 A US 5770175 A | | 04-09-1995 11-12-1996 05-08-1997 11-11-1997 23-06-1998 |
| US 5580540 | A 03-12-1996 | AU 1020297 A CA 2238059 A EP 0863844 A WO 9720769 A US 5683572 A | | 27-06-1997 12-06-1997 16-09-1998 12-06-1997 04-11-1997 |